

FUTURE COILS FOR ETHYLENE FURNACES: REDUCED OR NO COKING AND INCREASED COIL LONGEVITY

Marvin G. McKimpson^a and Lyle F. Albright^b

^aInstitute of Materials Processing
Michigan Technological Institute
Houghton, MI 49931-1295

^bSchool of Chemical Engineering
Purdue University
West Lafayette, IN 47907-2100

Introduction

Significant improvements have occurred in reducing undesired coke production in ethylene furnaces and in increased longevity of the coils during the last 40 years and especially in the recent past. Filamentous coke which is catalyzed with nickel or iron is an excellent collection site for the coke formed by two distinctly different mechanisms (1). Inner surfaces of coils used in ethylene furnaces that are essentially free of nickel and iron do not produce these filaments. Baker and Chludzinski (2) have found that certain surfaces result in much lower levels of coke formation. Albright and Marek (3) found that the surface of metal had a large effect on the morphology of the coke; three distinct coking mechanisms produce coke deposits of very different character. The ability to collect coke or coke precursors is obviously an important factor relative to the amount of coke that eventually collects.

Coated Coils

In the last 5-10 years, several companies have publicized coils with inner surfaces that result in much reduced levels of coke formation. The following companies claim reduced coke deposits by factors of perhaps two to three: Alon Surface Technologies, Inc.; Westaim Surface Engineering Products; and Daido Steel (in cooperation with Royal Dutch/Shell Group). In all cases, rather thin coatings have been formed on the inner surfaces of high-alloy steels. These coatings have low concentrations of nickel, iron, and other metals that produce filamentous coke. It must be emphasized that at the high temperatures experienced in the coils that considerable diffusion of metal atoms occur in the walls of the coils and metal oxides form in the inner surfaces (4). In regular (non-coated) coils of high-alloy steels, the inner surfaces often become much enriched in oxides of chromium, manganese, aluminum, silicon, and titanium. Simultaneously, a sublayer enriched in iron and nickel forms. Claims have been made for these coils that the coatings are regenerated as the coil is used and as metal (or metal oxides, sulfides or carbides) are lost from the surface.

Additives

For many years, numerous additives have been mixed in relatively small amounts with the feedstocks to ethylene furnaces to reduce coke formation. Apparently in all cases, the additive changes the composition of the inner surfaces of the coil.

Compounds containing sulfur are widely used when ethane and propane are feedstocks. When naphthas and gas oils are feedstock, such additives are generally not needed since the feedstocks already contain adequate sulfur. Additives employed include hydrogen sulfide, dimethyl sulfide, dimethyl disulfide, mercaptans, etc. Although details are not known, these compounds decompose at the high temperatures releasing elemental sulfur. This sulfur plus other sulfur-containing intermediates react in part at least converting metal oxides on the surface to metal sulfides (5). Tests have shown that

hydrogen sulfide treatment of a coil that had just been decoked reduces coke formation immediately following decoking (6).

The following questions relative to sulfur compounds apparently have not been answered. (1) Which portions of the coil should be sulfided? Presumably the exit portion of the coil should be since here coking is most pronounced. (2) Can the method of introducing the compound be improved? In current methods, most sulfur is possibly freed and reacted before it reaches the exit end. Sulfide formation often contributes to reduced coil life.

Other additives have been reported, but explanations for the improvements are still needed. Several additives include:

- 1) Tin-silicon additive marketed by Chevron-Phillips. Presumably the surface of the coil is enriched with tin and silicon (probably as oxides).
- 2) An organo-phosphorus compound marketed by Nalco-Exxon is used in numerous furnaces plus at least two transferline exchangers (TLE's).
- 3) Technip Benelux have suggested a pretreatment that produces a silica layer on top of sulfur-treated metallic sublayer. Further dimethyldisulfide is continuously added.
- 4) SK Corp. provides an additive that forms an inner film containing silicon, chromium, and aluminum oxides plus alkali or alkali-earth metals. Alkali and alkali-earth metals have been reported to act as catalysts to promote the oxidation of coke (via carbon-steam reactions at high temperature).

A key question with all additives is can improved methods be developed to introduce the additive to the coil? The answer likely is yes.

Pretreated Coils

Nova Chemical Co. (7, 8) has reported that their pretreated coils often experience coke reductions by factors of 14-16 times. In one case, the time before decoking of a furnace using ethane-propane feedstock was extended to 520 days. One patent claims that chromium-manganese spinels are produced on the inner surfaces. Similar pretreatments were earlier investigated (9) and the data since analyzed (10). The stainless steels were pretreated with hydrogen-steam mixtures at 800-1000°C for extended periods of time. Nova's preferred conditions overlap those reported earlier.

The question, as yet unanswered, is why has coke formation been so greatly reduced as compared to other technologies just discussed. Two possible explanations are as follows: First, the coke and/or coke precursors fail to adhere to the pretreated surface. Examples were found earlier (9) of poor adherence. Second the pretreated surface act as a catalyst to promote gasification of the coke.

Longevity of Coils

The longevity of ethylene furnace coils is influenced by numerous factors, including furnace operating conditions, decoking practices and alloy selection. In many cases, coil service life is limited by carburization and localized tube wall thinning. Frequent and/or aggressive decoking practices appear to accelerate this carburization. An improved understanding of the inter-relationships between carburization and decoking is likely to be very useful for further extending coil life.

Alloy composition also has a substantial influence on coking characteristics and the coil longevity. Ethylene furnaces present some of the most severe operating conditions encountered anywhere in the chemical process industries. Coil materials experience coking, carburization, oxidation, creep and thermal cycling during service, and must be able to be welded for field installation. Over the last several decades, furnace temperatures have tended to rise, placing increasingly-stringent requirements on these coils.

Increasing coil longevity will require materials increasingly resistant to all of these phenomena but still exhibiting adequate fabricability. Most current coils are cast, fully austenitic modified HP alloys containing nominally 25 Cr and 35 Ni with “micro-alloying” additions of elements such as Nb, W, Ti, and Mo. This family of austenitic alloys, however, may be approaching its useful operating limits. Alloys with increased Cr and Ni contents show limited improvements in creep resistance and decreased melting points. Equally important, these alloys rely primarily on Cr coupled with low levels of Mn and Si to provide oxidation and carburization resistance. At higher temperatures, both increased rates of coking and the volatility of chromium oxides become a major concern.

Several groups, including Oak Ridge National Laboratory and Special Metals Corporation, are exploring alloys with higher aluminum contents. These materials have potential for higher melting temperatures, improved oxidation resistance, improved carburization resistance and reduced coking compared to current alloys. Ferritic oxide dispersion strengthened alloys such as Special Metal’s Incoloy® MA956 (Fe-20Cr-4.5 Al-0.5Ti-0.5Y₂O₃) also exhibit substantially higher creep resistance (11). Novel approaches such as clad tubes with a ferritic core and austenitic sheath are being considered to address concerns about material ductility and weldability. The current status of this work will be reviewed.

References

- (1) Albright, L.F.; Marek, J.C., *Ind. Eng. Chem. Res.*, **1988**, 27, 755.
- (2) Baker, R.T.K.; Chludzinski, J.J., *J. Catalysis*, **1980**, 64, 464.
- (3) Albright, L.F.; Marek, J.C., *Ind. Eng. Chem. Research*, **1988**, 27, 751.
- (4) Luan, T.C.; Eckert, R.E.; Albright, L.F., *Ind. Eng. Chem. Research* **2003**, 42, 4741.
- (5) Tsai, C.H.; Albright, L.F., *Industrial and Laboratory Pyrolysis*, ACS Symposium Series 32, L.F. Albright and B.L. Crynes, Eds., pp. 274-295, Amer. Chem. Soc., Washington, D.C., 1976.
- (6) Crynes, B.L.; Albright, L.F.; *Ind. Eng. Chem. Processes Design Develop.* **1969**, 8, 25.
- (7) Benum, L., Achieving Longer Furnace Runs at Nova Chemicals, Spring Meeting, AIChE, New Orleans, 2002.
- (8) Benum, L.C.; Oballa, M.C.; Petrone, S.S.A.; Chao, W., Canadian Patent Applic. 2, 355, 436, March 27, 2002.
- (9) Szechy, G.; Luan, T.C.; Albright, L.F., *Novel Production Methods for Ethylene*, L.F. Albright and B.L. Crynes, Eds., Chapt. 18, Marcel Dekker, Inc., New York, 1992.
- (10) Luan, T.C.; Eckert, R.E.; Albright, L.F., *Ind. Eng. Chem. Research* **2003**, 42, 4741.
- (11) Hosoya, K., et. al., Application of New Ethylene Furnace Tube—OxideDispersion Strengthened (ODS) Alloy, 13th Ethylene Forum, Baton Rouge, LA, 2001.